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Chemical Reactivity and Electronic Structure of Silicon Microclusters

by

D. A. Jelski, T. T. Rantala and Thomas F. George

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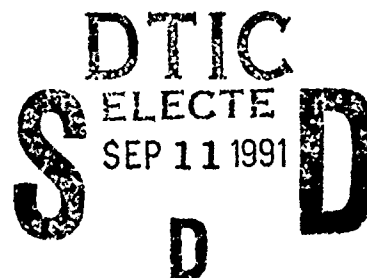
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19. ABSTRACT (Continue on reverse if necessary and identify by block number) The tight-binding model is used to study the structure and chemical reactivity of medium sized clusters, Si ₁₀ -Si ₆₀ . First, the validity of the model is established with a comparison to existing experimental and other calculated data. A new stable structure for the Si ₁₀ cluster is found. Second, the strong cluster size dependency in the reactivity with ammonia and methanol for Si ₃₀ ⁺ -Si ₄₅ ⁺ is modeled in terms of stacked, six-membered ring structures. This accounts for the periodicity of six in the reactivity pattern. Finally the photofragmentation of Si ₆₀ ⁺ indicating mainly Si ₁₀ ⁺ daughters is considered. It is suggested that Si ₆₀ consists of stacked ten-atom naphthalene-like rings.						
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CHEMICAL REACTIVITY AND ELECTRONIC STRUCTURE
OF SILICON MICROCLUSTERS

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1. Introduction

Small semiconductor clusters are of great interest both in fundamental science and applications. At present, however, both the basic properties and the kinetics behind the cluster formation are largely unknown. In supersonic beams where Si clusters can be grown, the random-like kinetics of Si atoms is suitable for growing small and large clusters with various structures. However, the experiments on these clusters show clear patterns, like periodicity in the reactivity and a photofragmentation pattern, which indicate the less random nature and properties of them. This obviously reflects the patterns in the conformation of the clusters with growing size.

We discuss here properties of small and medium sized Si clusters in light of our recent theoretical work. The topics we include are the structure, reactivity and photofragmentation, and in particular, the tight-binding (TB) model, which allows us to treat relatively large clusters compared to the possibilities of conventional *ab initio* methods. TB model has shown to be good for the treatment of electronic structure of bulk silicon, silicon surfaces¹ and small silicon clusters.² Also, it is a simple and transparent method, and it does not involve elaborate computations, comparable to conventional *ab initio* methods.

Our primary interest in using the TB model is twofold: First is the calibration of TB method, with an eye toward establishing the limits of applicability to medium sized clusters. Second is the elucidation of the structure of large silicon clusters, for which more sophisticated techniques are impractical. As our goals require comparison with both experiment and other calculations, we have chosen Si₁₀ as a model system since much data on the species already exists.¹⁻⁸ The treatment of large Si clusters is a straightforward application of the model,^{9,10} but the results are considerably more speculative given the absence of experimental data. Nevertheless, we will touch base with some important experimental parameters, and we believe that the results presented here are plausible.

For example, a dramatic variation in the reactivity of silicon clusters with

ammonia and methanol as a function of cluster size is observed.³ A periodicity in reactivity in units of six atoms is also observed, with Si_{36}^+ and Si_{42}^+ being most reactive, while Si_{39}^+ was less reactive by two orders of magnitude. Clearly, this variation cannot be attributed to cluster stability. Starting with a model proposed by Phillips,¹¹ we have tested the notion that clusters in this size range are arranged in stacked, six-membered rings, with the left-over atoms forming a cap.⁹

2. The Tight-Binding Model

The cohesion energy E_{coh} of a cluster is given as a sum of the band structure energy of electrons and an interatomic repulsion energy.²

$$E_{\text{coh}} = -(E_{BS} + E_R) \quad (1)$$

The band structure energy is defined as

$$E_{BS} = \sum_{\alpha} n_{\alpha} \epsilon_{\alpha} - \sum_{\beta} n_{\beta}^0 \epsilon_{\beta}^0 + U \sum_{\mu} (q_{\mu} - q_{\mu}^0)^2, \quad (2)$$

where the first two terms denote the sums over one-electron energies of the cluster, ϵ_{α} , and those of the isolated atoms, ϵ_{β}^0 , respectively. The third term is an intra-atomic Coulomb energy due to the charge transfer between the atomic sites μ .

The electronic levels of the cluster are solved from the TB (nearest-neighbor) Hamiltonian, with a basis set of four atomic levels (s, p_x, p_y, p_z). The diagonal elements of the s - and p -levels are -5.25 eV and 1.20 eV, respectively. The off-diagonal elements are assumed to vary as $1/r^2$, and for the equilibrium distance in the bulk material, 2.35 Å, their values are $V_{ss\sigma} = -1.938$ eV, $V_{sp\sigma} = 1.745$ eV, $V_{pp\sigma} = 3.050$ eV and $V_{pp\pi} = -1.075$ eV.¹ The net charge transfer required for the third term of Eq. (2) is calculated using a Mulliken population analysis, and $U \simeq 1$ eV.² The repulsion energy, E_R , consists of the sum of pairwise repulsive potentials, depending on the interatomic distance and the total number of bonds in the cluster.

We find that the one-electron levels are very sensitive to the geometry, and that very minute changes in the conformation cause large changes in the energy levels. For this reason, the minimization of the total energy through geometry

optimization is crucial. Therefore, we first use Hellmann-Feynman forces to come close to equilibrium, and then a multivariate minimization technique to optimize the structure without symmetry restrictions.

3. Structure of Si_{10} Clusters

First we consider three isomers of Si_{10} : *tetracapped triangular prism* (TTP), *bicapped tetragonal antiprism* (BTA) and *tetracapped octahedron* (TO), which have been suggested in literature^{4,6-8} to be the lowest energy conformations of Si_{10} . In addition, we find two stable but distorted BTA related structures, which we refer to as DBTA-I and DBTA-II, as illustrated in Fig. 1. The DBTA-I structure differs from the BTA in that it is stretched in one dimension and squeezed in another, and hence there is an additional bond (or a partial bond) with a bond length of about 3.30 Å. This reduces the symmetry of the species from D_{4d} to C_2 . DBTA-II contains no additional bonds, but involves a stretching and twisting of the original BTA form, also with C_2 symmetry. All BTA related structures are so called Jahn-Teller distortions (which lower the total energy) of more symmetrical species, and are stable in that there is a local energy minimum for each conformation. Obviously, the activation energy between them is very low.

Chelikowski *et al.*⁷ report the BTA structure as being most stable, whereas Ballone *et al.*⁶ cite TTP as the energy minimum. The *ab initio* calculations of Raghavachari⁴ result in either TO or TTP as the most stable structures. Raghavachari and Roling⁴ have investigated BTA in two different electronic configurations, but without the inclusion of the geometric effects of distortion. Within the accuracy of our calculation, the BTA and TTP forms appear to be degenerate, but neither matches the experimental photoelectron spectroscopy data. We also find that there is no band gap for BTA, but for TTP the HOMO-LUMO transition is 2.6 eV. The latter value is consistent with that obtained from more elaborate calculations reported for the same structure in Ref. 6. The experimental value observed by Cheshnovski *et al.*⁵ is, however, 1.2 eV. As is shown in Table I, our value for the band gap of DBTA-I is 1.4 eV, which closely matches this experimental result.

It is interesting to note that, with the exception of DBTA-I, all stable structures contain 24 bonds, or have an average coordination number of 4.8. This is to be compared with the bulk value of four. The adamantane structure is a 10-atom fragment of bulk solid, and it is relatively open rather than close packed. As a result, it has an average coordination number 2.4, only half that of the other structures. Our calculation agrees with the results of Ref. 2 in that we find the adamantane term of the 10-atom cluster to be unstable. Geometric optimization rapidly leads to the formation of additional bonds.

The above results explain the reactivity results for Si_{10} .¹² Given the probable low activation energy between the BTA-related forms, it should be useful to lump them together as one species. We have estimated the electron affinity of each isomer by listing the energy of the LUMO level in Table I. This is an indication of the propensity of the isomer to accept an additional electron, i.e., the lower the LUMO level, the greater the electron affinity. Similarly, a small HOMO-LUMO gap indicates a greater reactivity, since this implies that valence electrons have a greater freedom to rearrange in bond formation. It can be seen from Table I that the BTA-related structures have a greater electron affinity and a smaller band gap, implying that they are relatively reactive. Conversely, TTP has a low electron affinity, indicating low reactivity. Thus the reactivity results of Ref. 12 can be explained by concluding that two isomers of Si_{10} exist, with the more common (85 % abundance) being approximately an order of magnitude more reactive than the other.

4. Reactivity of Si_{30} - Si_{45} Clusters

A periodic reactivity pattern of silicon clusters has been reported.⁵ The reactions appear to be chemisorption, and it is unclear whether they are dissociative or not. We start our analysis by noting that the cluster stability does not necessarily have much to do with the reactivity. The former is thermodynamic whereas the latter is kinetic effect. Instead, the reasons for the variation in reactivity are mainly expected to be in the electronic structure: the charge distribution across the cluster, open shells (partly occupied HOMO) or dangling bonds. The electronic structure,

of course, is then expected to have a strong interplay with the conformation.

Here we present two possible models for the correlation between the charge distribution and the observed periodic reactivity pattern. Beginning with Phillips' hypothesis, that silicon clusters are arranged in stacked, six-numbered rings, we have calculated the most stable geometries and the charge distributions by minimizing the cohesion energy in Eq. (1). The clusters which we have investigated are all singly-charged cations, ranging in size from $n = 25$ to $n = 45$.

We find that all clusters can assume a cylindrical shape in that there is a local energy minimum near these geometries. There may, of course, be many other stable (possibly more stable) configurations. Evidence for the actual existence of the cylindrical shape, therefore, stems from the reactivity pattern, and not necessarily from the cluster stability. We find that the cohesion energy per atom for all clusters from $n = 25 - 4$ is between 3.1 eV and 3.5 eV, i.e., within a few tenths of an electron volt. Since our calculation is relatively primitive, we do not believe the differences to be significant, and this is consistent with the experimental observation that all clusters appeared in equal abundance.

The most apparent aspect about the geometry is the flatness of the rings. This, along with the fact that the intra-planar distance is frequently smaller than the distance between planes, suggests that the rings are slightly conjugated. This hypothesis is borne out by a calculation of the bond orders: the bond order between ring atoms ranges around 1.10, whereas the bond order between planes is closer to 0.90.

As illustrated by Fig. 2a (the other clusters look very similar), the atoms in the "body" of the cluster are tetrahedrally coordinated, as in the bulk, through the shape is altered due to strain. The atoms at the end tend to be triply coordinated, though the existence of the cap complicates that generalization. In any case, it is obvious that there are a large number of dangling bonds per molecule, but in our calculation we find no significant variation in the number of dangling bonds as a function of cluster size. However, Si_{36}^+ is found to have the fewest dangling bonds,

as one would expect due to the higher degree of symmetry (no cap). Thus, the experimental result that all species react rapidly with free radicals, such as NO, is clearly accommodated by this model, as one would suppose that free radicals would react with dangling bonds.

Of greater significance is the charge distribution within the cluster. Despite all clusters being singly-charged cations, we can see from Fig. 3 that there is a significant variation in charge density within the cluster. For Si_{36}^+ , the molecule is symmetric and the positive charge is concentrated at each end. The center of the cluster is negatively charged, which is consistent with the notion that the rings are slightly conjugated, and thus able to support an additional number of electrons.

Recently, we have carefully investigated the structure of Si_{45} cluster,¹³ which was experimentally found unreactive like Si_{39} . It turns out that a highly symmetric tetrahedral conformation, as illustrated in Fig. 4, exists, whose properties clearly indicate inertness. Firstly, this Si_{45} isomer is very stable which implies large abundance. Secondly, its closed shell electronic structure together with a high coordination number (more than four, resulting from 96 bonds) reduces the number of dangling bonds and leads to a large HOMO-LUMO gap. This explains the inertness in chemical reactions very nicely. And finally, this conformation still accommodates the periodic reactivity pattern in that it is possible to remove a "six-atom ring" from the tetrahedral Si_{45} resulting in a Si_{39} (Fig. 2b) with the same "inert" features in the electronic structure as those of Si_{45} .

A suggested conformation for Si_{39} is shown in Fig. 2. An additional structure may be derived by removing one of the six-membered rings from Si_{45} (Fig. 4), leaving the cluster with approximate triangular pyramidal geometry. We note that it is impossible to make a tetrahedral cluster from 39 atoms, and therefore any lack of reactivity observed in Si_{39} must be due to some other pattern. The sequential removal of six-membered rings seems to be a logical guess, though the periodic reactivity pattern has also been disputed recently.¹⁴

5. Photofragmentation of Large Silicon Clusters

When Si_{60}^+ is fragmented with an ArF laser,¹⁵ almost all daughter fragments are in the 6-11 atom range. A smaller amount fragments by losing one atom, yielding an Si_{59}^+ cluster. The laser intensity dependence indicates that this may be a two photon process. Of the smaller fragments, Si_{10}^+ is the most common. Because any charge will tend to form on the larger daughter, the absence of any larger charged clusters probably indicates that they are not formed at all, rather than being neutral and hence undetected. The experimenters report that other clusters also fragment into 10-atom pieces, where most notably Si_{10}^+ is almost exclusively the daughter fragment.

The obvious extension of our structural hypothesis outlined in the previous section is to suppose that Si_{60} consists of naphthalene-like planes, as illustrated in Fig. 5. Note that most atoms are tetra-coordinated. Those on the top and bottom have only three nearest neighbors, whereas those in the middle have five. The charge density is distributed within the planes to reflect this, i.e., less coordinated atoms are more positively charged, whereas atoms in the middle of the cluster are better able to neutralize charge, and thus are more negative. The cohesion energy of the Si_{60} cluster is 3.6 eV. This compares with a bulk cohesion energy of 4.6 eV, and that of Si_{10} of about 3.9 eV.^{2,4,8}

For clusters of intermediate size, the close-packed structure is not possible. Surface effects prevent the stability of the bulk lattice. So the cohesion energy is lower than either the 10-atom cluster or the bulk. For comparison, we have performed a similar analysis of Si_{60} as a bulk fragment arranged as spherically as possible to minimize surface energy. The cohesion energy for this structure is found to be 3.2 eV.

To compare with experimental fragmentation data, we have calculated the bond orders, which describe the strength of the bonds and are reported in Fig. 6. The strongest bonds in a given plane are those marked o. This strength is due to the conjugated nature of the rings and the fact that the atoms in this group

are no more than tetra-coordinated. The next strongest bonds are those marked x. These involve atoms with higher coordination numbers, requiring the sharing of electrons over additional bonds. The average value of the 1-6 bond taken alone is 0.137 eV. Finally, the weakest bonds are between the planes. The fragmentation of the cluster into 10-atom pieces is supported by this result.

The explosive nature of the fragmentation is not revealed by the average figures. In Fig. 6b we illustrate the average bond strength connecting each of the layers. It can be seen that the bond strength parallels the charge density distribution. The atoms at each end contribute electrons to their neighbors, and hence the bonds between the extreme planes and those just inside are strong. Similarly, the electron density is small in the center of the molecule, and so the bond between planes 3 and 4 is also strong. The weakest bonds are found between planes 2, 3 and 4, 5. Thus any fragmentation of the molecule is likely along these lines, and we are left with three, 20-atom fragments.

We believe that the above model accounts for the photofragmentation data better than any other proposed structure, but it fails to account for most other data. The photofragmentation effect appears universal across the entire spectrum of silicon clusters, from 20 atoms and larger, that any model to describe it must either be independent of the geometry of the parent cluster, or suppose some consistent geometry. We are increasingly drawn toward the former premise. It seems improbable that clusters of such a wide size range would have similar geometries and yet be dramatically different in other respects. We therefore come reluctantly to the conclusion that the photofragmentation data yields little or no information about the structure of the parent ion.

Instead, to our opinion the photofragmentation data can be better explained by fragmentation kinetics and properties of daughter clusters. Very small clusters (three or four atoms) are too small to have large coordination numbers, and therefore are very reactive. Thus it may be that large clusters are broken apart into small pieces, but that these rapidly react with each other to form the highly-coordinated

Si₁₀ species. It is not therefore, that Si₁₀ is exceptionally stable or that 10-atom fragments are hidden in every cluster, but rather that it is relatively unreactive.

6. Summary .

We have found that a distorted form of the bicapped tetragonal antiprism (DBTA) is the most stable structure for the Si₁₀ cluster. In addition, the HOMO-LUMO "band gap" and electron affinity data correspond with experiment. We view this as a justification of our original hypothesis, namely that the TB model, optimized for a solid and a dimer, can be used for medium sized clusters. Our results are consistent with previous work, most notably with Ref. 7, in which BTA is proposed as the stable configuration for Si₁₀.

The reasons behind the observed periodic reactivity pattern of silicon clusters may be several-fold. Basically the reactivity is a property of the electronic structure, which then also reflects the conformation (geometry) of the cluster. In this spirit we have presented two possible models for the reactivity (or inertness), of which we prefer the one emphasizing the role of dangling bonds and the HOMO-LUMO gap.

Concerning the interesting photofragmentation data which show that the daughter clusters are mainly 10-atom fragments, we offer a new and alternative explanation. Because the relative abundance of 10-atom clusters is large and independent of the parent clusters, we conclude that the fragmentation kinetics together with the properties (inertness) of daughters rather than the properties of the parents is the essential factor in the observed photofragmentation pattern.

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TABLE I

Species	Cohesion Energy (eV/atom)	HOMO-LUMO gap (eV)	LUMO level (eV)
DBTA-I	-3.98	1.4	+0.18
DBTA-II	-3.92	0.6	-0.50
BTA	-3.90	0.0	
TTP	-3.91	2.6	+1.21
TO	-3.61	2.9	+2.00

Table I The cohesion energies, HOMO-LUMO transition energies and LUMO energies of the various Si_{10} structures shown in Fig. 1. The LUMO one-electron energy, which is a rough indication of the electron affinity, is given relative to the "HOMO" level of the bulk.

FIGURE CAPTIONS

Figure 1. Structures for the (a) TA, (b) TTP, (c) TO, (d) DBTA-I and (e) DBTA-II clusters, with distances in Å. The atoms with hatch marks are the caps.

Figure 2. A model of Si_{39} composed from the stacked six-numbered rings.

Figure 3. Total electronic charge per layer for different silicon clusters. The diagrams on the left of each figure represent a schema of the cluster geometry, with the solid bars denoting a six-membered ring, and the individual atoms of the cap are shown explicitly. The bar graphs on the right show the total charge per layer, i.e. the sum of the charges of each atom constituting a single layer.

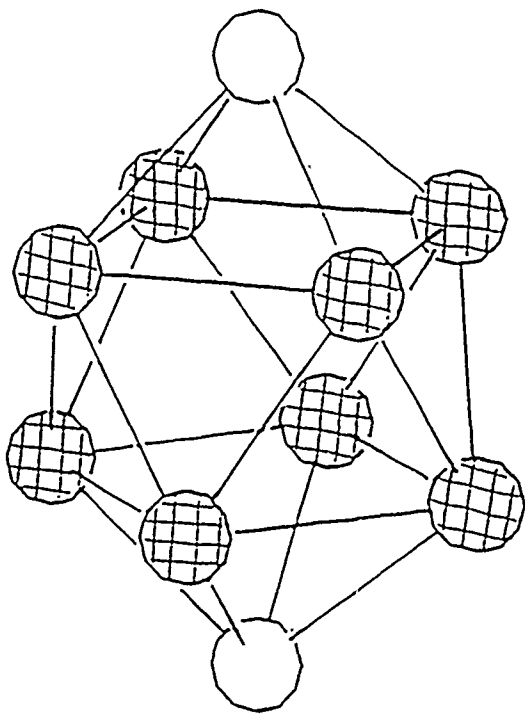
Figure 4. The tetrahedral model of Si_{45} from Ref. 13.

Figure 5. Proposed structure for the Si_{60} cluster, consisting of six stacked, 10-atom naphthalene-like rings.

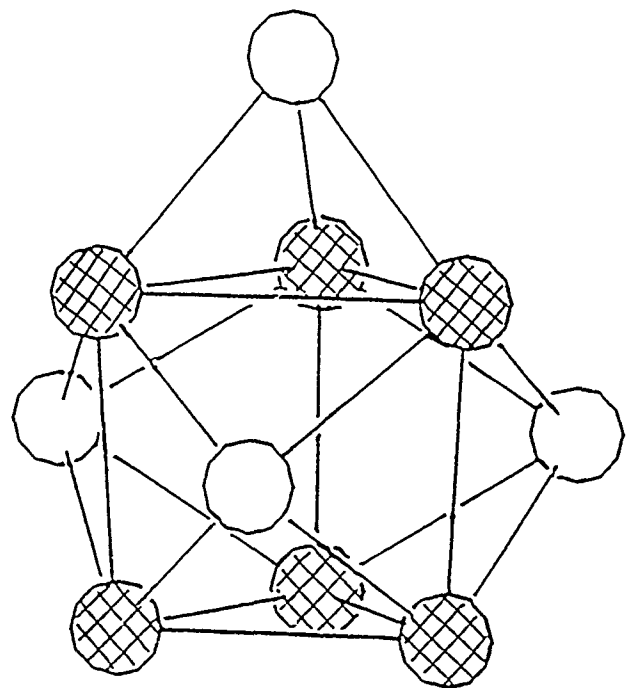
Figure 6.

- (a) Average relative bond strength (bond order) for different categories of bonds within the proposed Si_{60} cluster.
- (b) Average relative bond strength of the bonds between each of the planes in the proposed Si_{60} cluster. Each number is an average over 10 bonds.

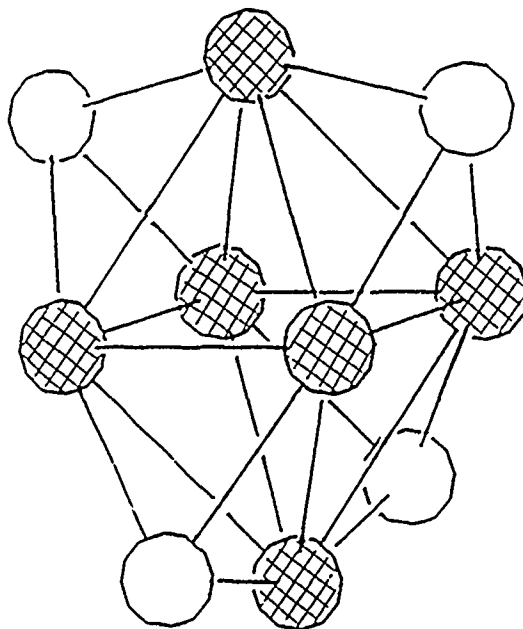
Fig. 1 (a) - (c)



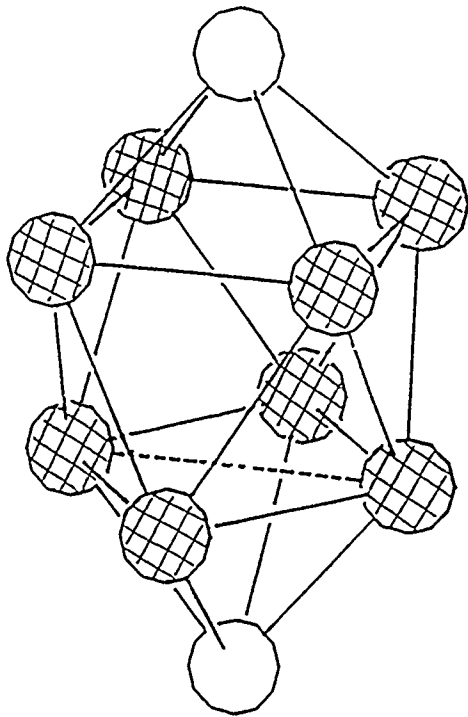
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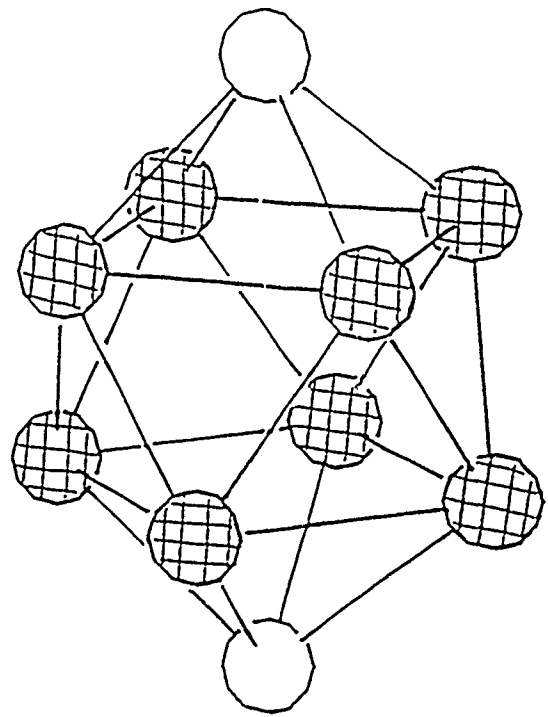
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(e)

Fig. 2

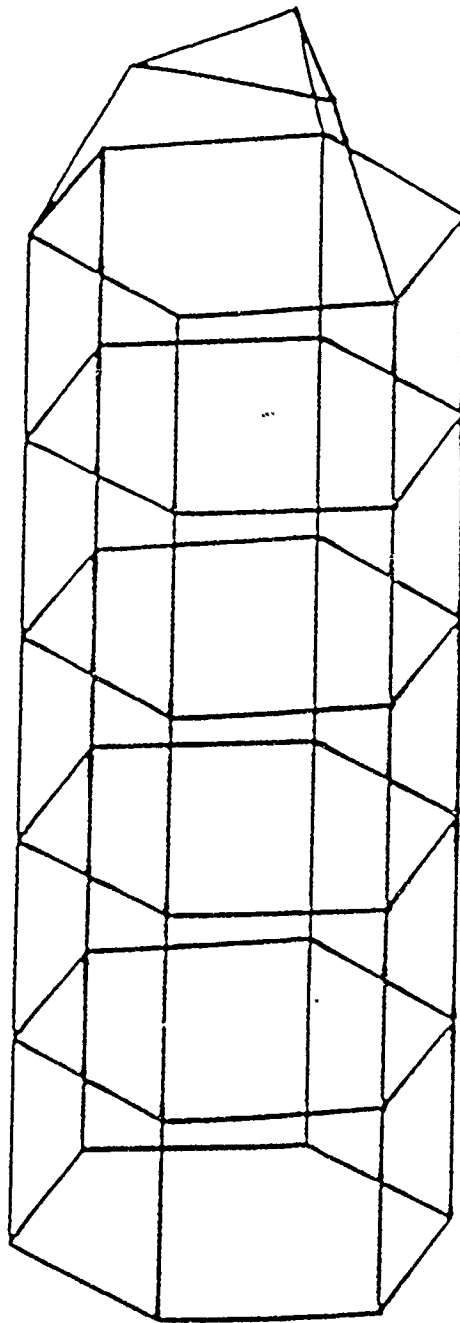


Fig. 3

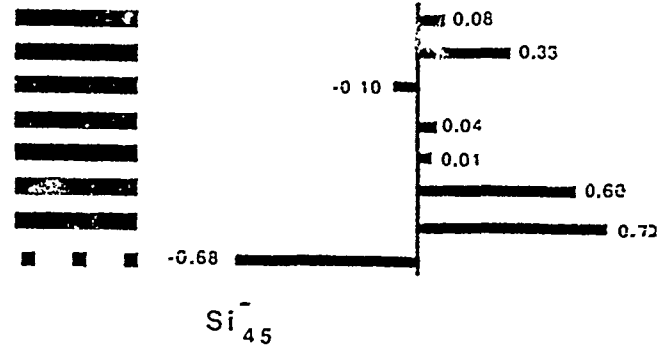
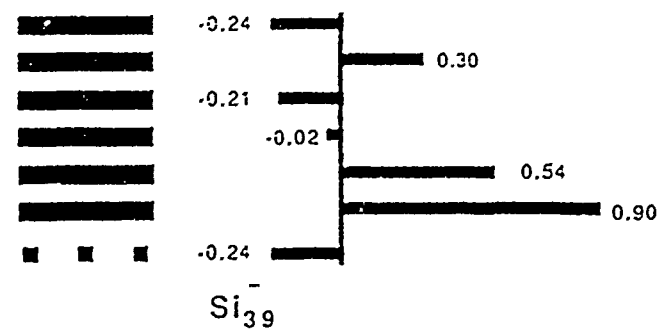
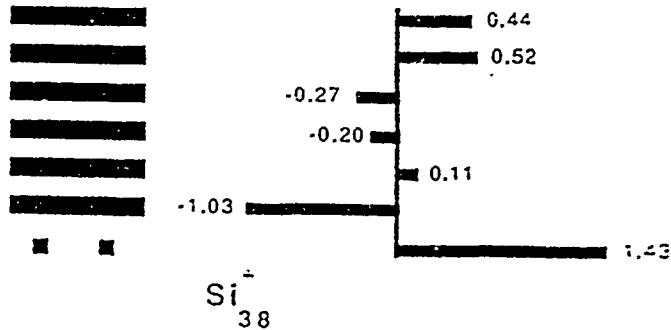
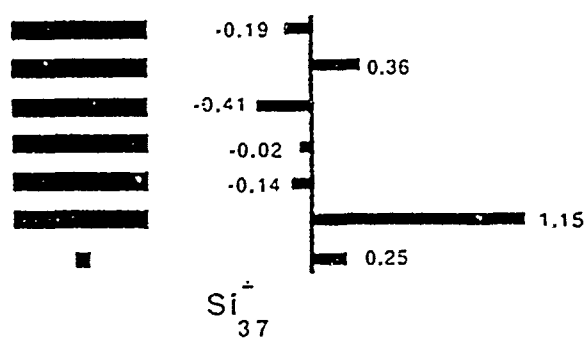
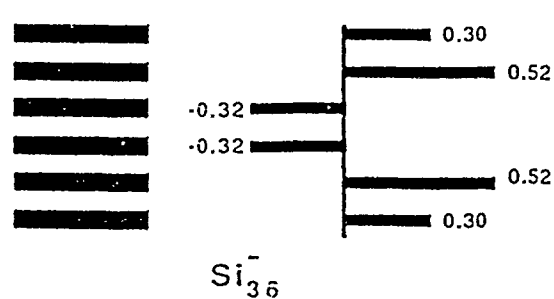
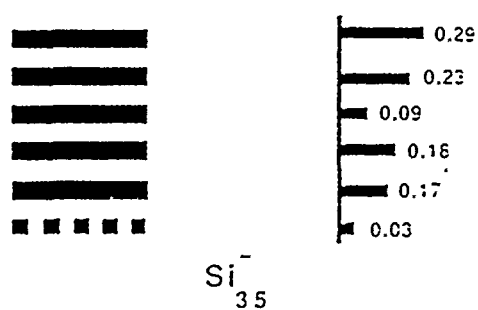
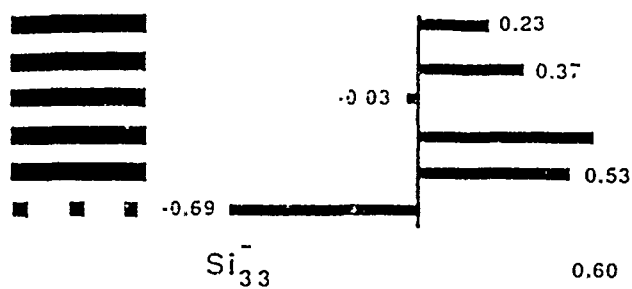


Fig. 4

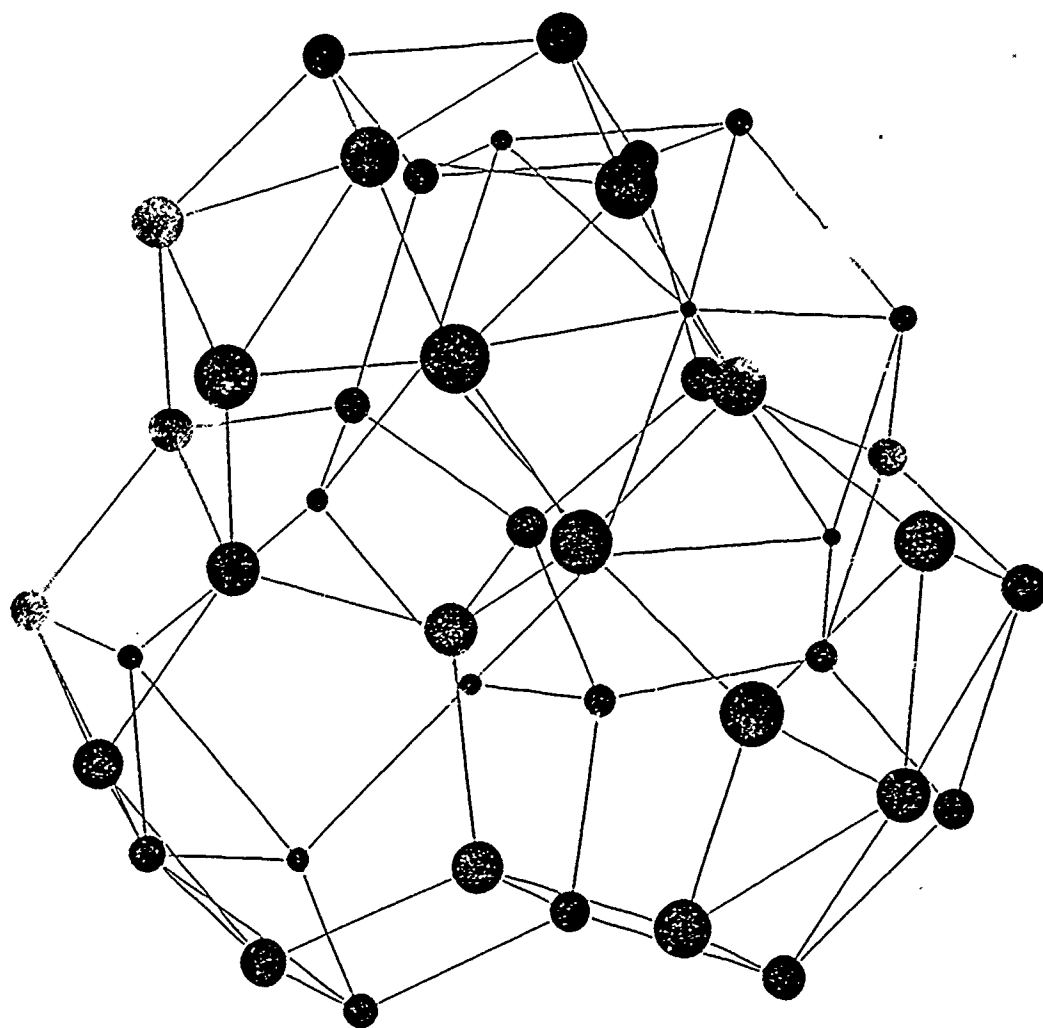


Fig. 5

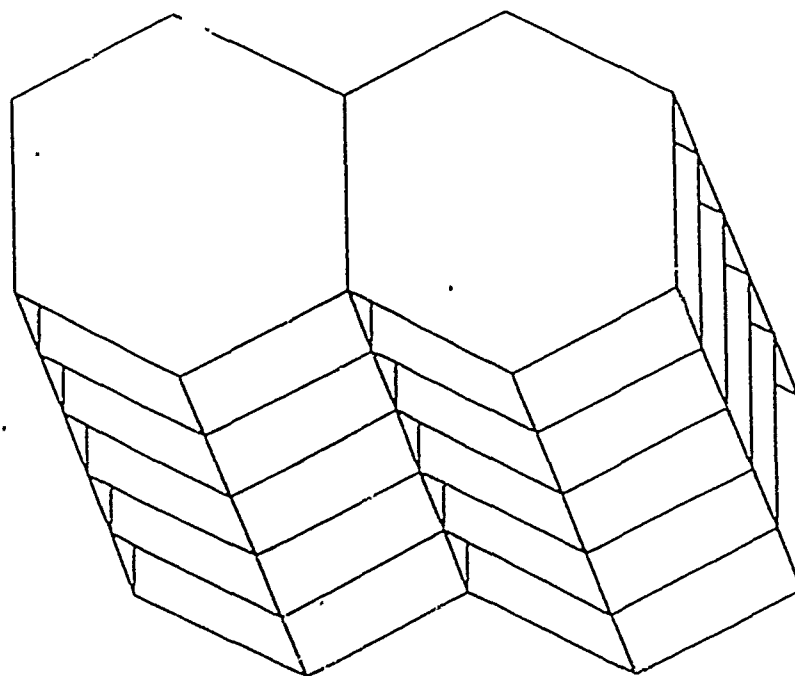
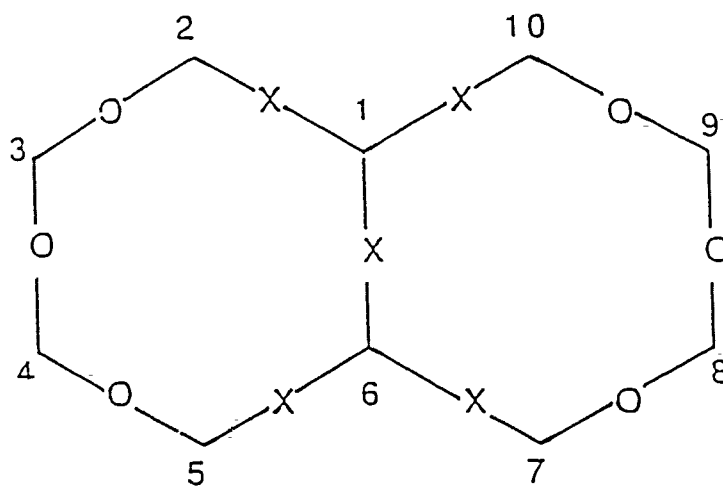


Fig. 5



(a)

O : 0.185

X : 0.146

(b)

0.171

0.104

0.147

0.104

0.171